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Effect of n-type Doping on the Hole Transport in Poly(p-phenylene vinylene)

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ABSTRACT: N-type doping of poly(2-methoxy-5-(2′-ethyl-hexyloxy)-p-phenylene vinylene) (MEH-PPV) with decamethylcobaltocene (DMC) strongly improves the electron transport due to filling of the electron traps. Unexpectedly, the n-type doping simultaneously suppresses the hole transport in MEH-PPV. We demonstrate that this strong reduction of the hole transport originates from unionized DMC molecules that act as hole traps. This hole trapping effect explains why the current of a DMC-doped MEH-PPV polymer light-emitting diode is orders of magnitude lower than that of the undoped device. © 2011 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 49: 1745–1749, 2011

KEYWORDS: charge transport; molecular doping; organic semiconductors; polymer light-emitting diodes

INTRODUCTION Polymeric semiconductors are promising candidates for a number of applications because of their ease of processing and therefore potential low-cost production. Polymer materials can be used for fabricating flexible large-area light sources like flat panel displays. In many light-emitting polymers, such as poly(2-methoxy-5-(2′-ethyl-hexyloxy)-*p*-phenylene vinylene) (MEH-PPV) and poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO-PPV) electron and hole currents are highly unbalanced. The hole transport in poly(*p*-phenylene vinylene) (PPV) based polymer light-emitting diodes (PLEDs) is determined by a space-charge-limited current, showing a quadratic dependence on voltage. The electron current, however, is orders of magnitude lower than the hole current and depends on the applied bias voltage more strongly, which is attributed to the presence of electron traps in the polymer.[1,2] Therefore, in a PLED, the current is governed by the hole transport. As a consequence, the excitons are mainly formed near the cathode. It has been demonstrated that within 10 nm of the metallic cathode, the excitons may recombine through a nonradiative decay process.[3] As a result, at low voltages, the device efficiency is largely limited by this quenching process.

To achieve a more balanced charge transport in a PLED, the improvement of the electron transport is essential. It has been shown that the charge transport of polymers can be improved through doping. So far, a number of approaches have been investigated, especially for p-type doping. For example, the hole current of a conjugated polymer can be increased by two orders of magnitude upon the addition of tetracyano-tetrafluoro-quinodimethane (F4TCNQ).[4,5] Until now, n-type doping for organic materials is still a challenge. Donating electrons to the lowest unoccupied molecular orbital (LUMO) of the polymer requires a dopant molecule having an extremely low ionization energy (IE). Therefore, most n-type dopants are susceptible to oxidation in ambient air,[6] so that water and oxygen are detrimental for a n-doped device. There are several approaches to achieve n-type doping, for example with alkali metals and their derivatives, such as Li,[7,8] LiF,[9] Cs,[10] and Cs_2CO_3.[11] However, their small size may cause them to drift under the applied electric field.[8,12,13] Recently, Chan et al. reported on a novel n-dopant, decamethylcobaltocene (DMC), which has an IE as low as 3.3 eV.[14] The large size of this organic compound makes it less mobile in the organic film. DMC was shown to be an efficient n-dopant for small organic molecules such as copper phthalocyanine[14] and pentacene.[15] In polymers like PPV derivatives, however, the IE of DMC is not sufficiently low to enable electron transfer to the LUMO, typically 2.9 eV for MEH-PPV. Despite this fact, it has been demonstrated that the electron current can be strongly increased. Instead of generating free electrons, the dopant molecules fill the electron traps in the polymer, causing deactivation of these traps and thereby enabling the measurement of a trap-free electron current.[16] After doping, the trap-free electron and hole transport were observed to be equal, demonstrating that in MEH-PPV the electron and hole mobility are identical. As a result the effect

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of p- and n-type doping on the transport of majority carriers in conjugated polymers has been extensively studied in recent years.

A problem that is characteristic for p- and n-type doping using solution processable semiconductors is that only a small fraction of the dopants, typically a few percent,[5,16] is ionized. A fundamental question is whether the large fraction of unionized doping also influences the transport of the minority carriers. In classical inorganic semiconductors, minority carriers play an important role in, for example, bipolar transistors and solar cells. Furthermore, their ability to form an inversion layer in field-effect transistors is the cornerstone of silicon based electronics. Here we study the effect of n-type doping on the hole transport in MEH-PPV. It is demonstrated that the large amount of unionized dopant molecules act as hole traps. So next to a strongly enhanced current of the majority carriers (electrons), the addition of n-type doping simultaneously suppresses the current of the minority carriers (holes) in conjugated polymers. As a result, it is difficult to achieve balanced transport in a conjugated polymer by doping. This trapping effect of unionized dopants is relevant for understanding the physics of doped organic devices where minority carriers play a role, including Schotkky barriers and p-n junctions.

EXPERIMENTAL

First, poly(3,4-ethylenedioxythiophene):poly(4-styrene sulphonate) (PEDOT:PSS) was spin casted on indium tin oxide (ITO) prepaterned glass substrates as the bottom electrode. MEH-PPV was dissolved in toluene with a concentration of 4 mg/mL and DMC was dissolved in N-methyl-2-pyrrolidone (NMP) with a concentration of 10 mg/mL. Both the dopant and the polymer solutions were stirred at 70 °C for 12 h and subsequently cooled down to room temperature. The solutions were filtered with 0.5-μm pore size polytetrafluoroethylene (PTFE) filters, respectively. By using a 10-μL volumetric pipette, the blending of the dopant solution in the polymer solution can be precisely controlled. After stirring at room temperature for 2 h, the blend solution was spin casted without further filtering. Because of the high boiling point of NMP (202 °C), the polymer films were kept in a vacuum chamber for 12 h to ensure that no residue of the solvents existed in the polymer layer. Barium (Ba) and aluminum (Al) were deposited as top electrodes for the PLEDs by thermal evaporation through a shadow mask under a chamber pressure of 1×10^{-7} mbar. In hole-only devices, polymer thin-films (undoped and doped) were sandwiched between a PEDOT:PSS covered ITO anode and an gold (Au) cathode. Electron-only devices with MEH-PPV sandwiched between an Al anode and a Ba/Al cathode were fabricated in the same batch for comparison. The current density–voltage (*J–V*) characteristics of the devices were measured using a Keithley 2400 source meter in a nitrogen atmosphere. The light output was recorded simultaneously using a calibrated Si photodiode connected to a Keithley 6514 electrometer.

RESULTS AND DISCUSSION

As stated above in solution processable semiconductors, only a small fraction of the dopants of only a few percent[5,16] is ionized. To investigate whether the large fraction of unionized doping plays a role in the minority carrier transport we prepared electron-only, hole-only, and PLEDs with an n-doped emissive layer. Similar to previous results,[16] after doping, a strong improvement in the electron transport was observed (Fig. 1): The measured current density of the doped device is two orders of magnitude higher than that of the undoped device. It has been demonstrated that for sufficiently high doping concentrations the enhanced electron current is equal to the trap-free SCLC as measured in hole-only devices.[16] This shows that all electron traps in the MEH-PPV can be filled by electrons originating from the ionized dopants. Furthermore, in MEH-PPV, a hysteresis effect is commonly observed on the first *J–V* sweep of an electron-only device,[17] because of the deep electron traps. Since the trapped electrons that accumulated during the up-scan cannot be released promptly, they will influence the following down-scan, resulting in an irreversible hysteresis effect. However, in the *J–V* plot of a doped device, the hysteresis disappears completely, also confirming that all the deep traps in the polymer are filled by the dopant molecules (Fig. 1). Under reverse bias, no device current can be measured from the undoped device, due to the electron injection barrier at the Al bottom electrode. The doped device shows equally high currents under forward and reverse bias. This is caused by doping inducing charge dipoles on the polymer/metal interface, which reduces the injection barrier.[18,19] With the observed enhancement of the electron transport upon doping, the electron and hole transport in DMC-doped MEH-PPV based PLEDs is expected to become more balanced. However, this expectation is based on the assumption that the n-type doping does not affect the hole transport.

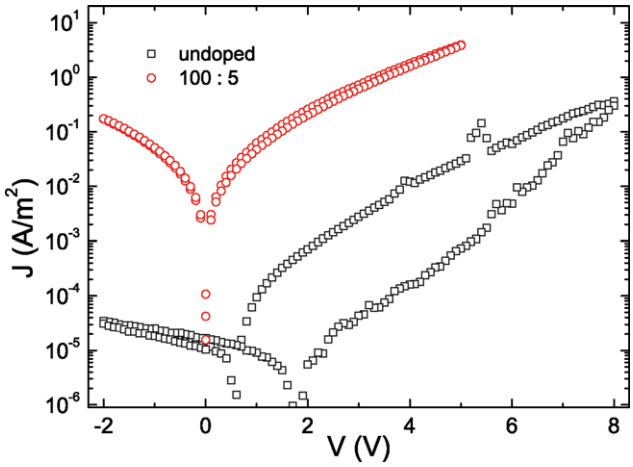

FIGURE 1 *J–V* characteristics of undoped and DMC-doped MEH-PPV electron-only devices. The doping ratio is 100:5 (by weight). All devices have the same thickness: 130 nm.

To study the influence of DMC on the hole transport of the polymer, hole-only devices were fabricated. It was observed that the measured device current scales inversely with the doping concentration, where the undoped device shows the

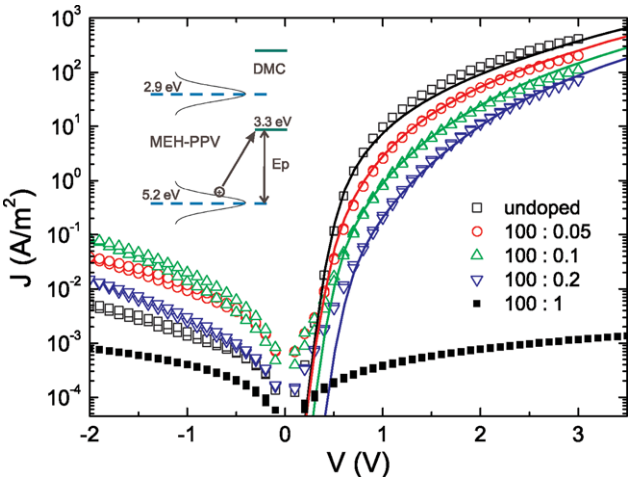

FIGURE 2 Open symbols represent the *J–V* characteristics of undoped and DMC-doped MEH-PPV hole-only devices with different weight ratios. All the devices have the same thickness: 80 nm. The solid lines represent the prediction of the device model. Solid symbols represent the *J–V* characteristics of DMC-doped MDMO-PPV (100:1 by weight) hole-only device with a layer thickness of 175 nm. The inset shows the energy diagram of trapping mechanism.

highest current (Fig. 2). Moreover, for a doping concentration larger than 1%, no current could be measured in a hole-only device. Apparently, while the addition of the n-type dopant greatly improves the electron transport, its presence is detrimental for the hole transport. This can be explained by the formation of a trap-limited current, where the origin of the traps is illustrated in the energy diagram shown in the inset of Figure 2. The IE of DMC (3.3 eV) is 0.4 eV deeper than the LUMO level of MEH-PPV (2.9 eV). This energy barrier prevents a complete charge transfer from the dopant to the host at room temperature. Therefore, only part of the dopant molecules are ionized and fill the traps in the polymer, whereas the other part remains unionized. It has been shown that for a DMC-doped MEH-PPV system the doping efficiency is only 1%,[16] which implies that 99% of the dopant molecules are charge neutral. The unionized dopant molecules can act as deep hole traps and therefore hamper the hole transport. Possible reasons that account for the low doping efficiency are: (i) ineffective charge transfer between the dopant and the host; (ii) aggregation of the dopant molecules in solution or in the film after deposition.

Although the current decreases with increasing doping concentration, the shape of the *J–V*s are still similar to that of the undoped device, characteristic for a trap-limited current with a single energy trap level. If we assume that the trap density is much larger than the charge carrier density, a simple approximation of the current density in a single carrier device with traps confined in single discrete energy levels leads to[20]

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\theta\frac{(V-V_{bi})^2}{L^3}, \quad (1)$$

where $\varepsilon_0\varepsilon_r$ is the dielectric constant, μ the mobility, V the applied bias voltage, V_{bi} the built-in potential, and L the active layer thickness. This equation is the well-known Mott-Gurney square law[21] multiplied with a factor θ, which is the ratio between the free carrier density and the total carrier density, according to

$$\theta = \frac{p}{p+p_t}, \quad (2)$$

where p and p_t are the free and trapped hole density, respectively. This formula indicates that the trap-limited current is lower than the trap free current, while the shape of the *J–V*s remains same. This is in line with what is observed from the measurements shown in Figure 2. The approximation of equation 1 assumes that the mobility is constant over the full voltage range. However, when the applied electric field[22] and the charge carrier density[23,24] are considerably large, this assumption is not valid anymore. To study the properties of the traps in depth, the experimental data were fitted with a numerical drift-diffusion device model.[25] First, the undoped MEH-PPV hole-only devices are modeled. To characterize the charge transport of the doped devices, a single-level hole trap is introduced in the model, representing the "unionized" DMC molecules. Here, two parameters are involved to describe the traps, the trap density (P_t) and the trap energy (E_t). Figure 2 displays the experimental and simulated *J–V* characteristics of the undoped and doped hole-only devices. Assuming that the density of the polymer, as well as of the dopant, is equal to 1 mg/mL, with a doping ratio of 100:0.05 (by weight) the doping concentration is around 10^{24} m^{-3}. By comparing the doping concentration with the estimated trap density, we can conclude that around 3% of the dopants are acting as hole traps. The estimated trap densities are plotted against the doping concentrations in Figure 3. With increasing doping concentration, a clear trend of increasing P_t is observed, as expected. This behavior does not have to be strictly linear, because the dopant molecules may form clusters in the solution as well as in the polymer matrix. How many electrons one cluster can donate is unknown.

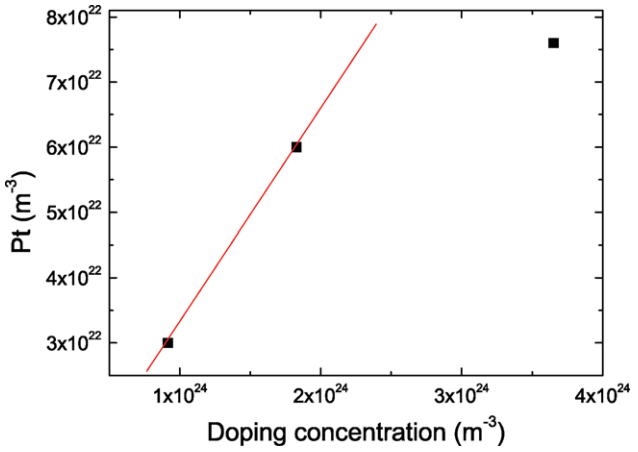

FIGURE 3 The trap density (P_t) as a function of the n-type doping concentration.

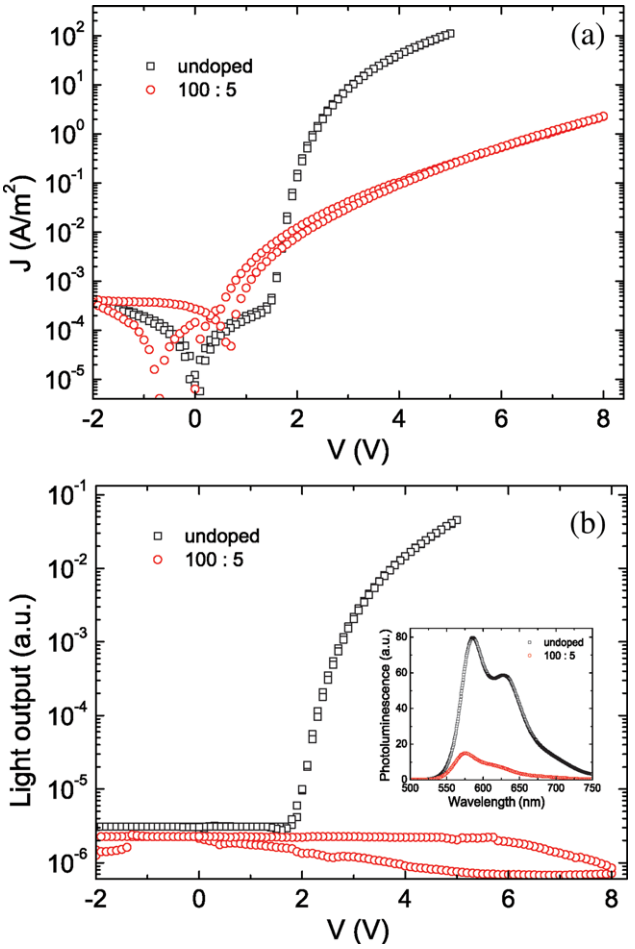

FIGURE 4 (a) *J–V* characteristics and (b) luminance-voltage characteristics of undoped and DMC-doped MEH-PPV LEDs (100:5 by weight). All devices have the same thickness: 130 nm. The inset of (b) shows the photoluminescence spectra of undoped and DMC-doped MEH-PPV thin films.

From the numerical simulation, the estimated E_t amounts to 0.45 eV. Considering the difference between the highest occupied molecular orbital level of the polymer (5.2 eV) and the IE of the dopant (3.3 eV), the hole traps should be very deep (1.9 eV). The *Et* estimated from the numerical simulation is much smaller. One possible reason is that the estimated shallow trap levels may originate from the DMC^+ ions, as the second ionization potential of DMC still locates within the band gap of MEH-PPV. It should be noted that for a single-level shallow trap in a band-like semiconductor, the ratio θ is given by

$$\theta = \frac{n}{n+n_t} = \frac{N_C}{N_t}\exp\left(-\frac{E_t}{kT}\right), \quad (3)$$

where N_C is the effective density of states (DOS) of the band, N_t the number of trap sites, and E_t the trap depth. However, for strongly disordered semiconductors the transport sites have a Gaussian distribution of energies (DOS), characterized by an energy width σ.[22] In such a disordered system the ratio θ between free and trapped carriers in case of a shallow trap is then given by

$$\theta = \frac{N}{N_t}\exp\left(\frac{1}{2}\left(\frac{\sigma}{kT}\right)^2 - \frac{E_t}{kT}\right) \quad (4)$$

with N the number of transport sites. As a result the derived trap energy from equation 3 is an effective trap energy that also contains the width of the DOS of the free carriers. In this case, the width of the Gaussian DOS distribution for MEH-PPV can be estimated from the simulation, which amounts to 0.104 eV. This number agrees with the value published previously.[2]

As expected, the introduction of the n-dopant in a PLED reduces the light output due to quenching of the excitons by the dopant [see Fig. 4(b) and the inset of Fig. 4(b)]. However, it was not expected beforehand that also the PLED current would be reduced by two orders of magnitude [Fig. 4(a)], since doping usually leads to an enhancement of the charge transport due to the additional charge carriers. As demonstrated in this study, the decrease of the current in a PLED is a direct consequence of the hole trapping by unionized dopants that reduces the total current. These results demonstrate that it is very difficult to achieve balanced charge transport in a conjugated polymer by doping. In state-of-the-art multilayer OLEDs from evaporated small molecules the n-type doped electron transport layer simultaneously acts as a hole blocking layer. In this way, the hole trapping effect of unionized n-type dopants, that is a typical problem for solution processed layers, is circumvented and balanced charge transport can be achieved.

CONCLUSIONS

We have studied the hole and the electron transport in n-doped polymer devices. The current in both the LEDs and the hole-only devices decreases, showing that the inactive n-type doping acts as hole traps and hampers the hole transport. By considering the trap level in the band gap of the polymer, the trap density and the trap energy can be estimated from the numerical simulation. Since the light output is also largely suppressed by quenching from the dopant, n-type doping can only be employed in electron transport layers that also block holes.

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